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Interfacial Fe(III)-hydroxide formation during Fe–Pt alloy deposition

K. Leistner[a,b,*], P. Schaaf[c], A. Voss[a], S. Fähler[a], L. Schultz[a,b], H. Schlörb[a]

[a] *IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany*
[b] *TU Dresden, Faculty of Mechanical Engineering, Institute of Material Science, 01062 Dresden, Germany*
[c] *Universität Göttingen, II. Physikalisches Institut, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany*

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Abstract

Fe–Pt films with an Fe/Pt ratio close to one can be electrodeposited from an $FeSO_4$–H_2PtCl_6–Na_2SO_4electrolyte. At the deposition potential, the hydrogen evolution and the reduction of the Pt complex are diffusion limited, and Fe overpotential deposition has not yet set in. The sources of the Fe incorporation are iron hydroxide formation together with Fe underpotential deposition due to Fe–Pt alloy formation. Mössbauer measurements show that the iron in the iron hydroxide is predominantly Fe(III). For stoichiometry reasons, a Pt-rich Fe–Pt phase must be present in addition to the Fe(III)-hydroxide. The Fe^{3+} that takes part in the hydroxide formation is produced in the electrolyte by the oxidation of Fe^{2+} by the complexed Pt ion. This exchange reaction results in a significantly higher Fe^{3+} content in the $FeSO_4$–H_2PtCl_6–Na_2SO_4 electrolyte in comparison to the same electrolyte without H_2PtCl_6. Fe(III)-hydroxide formation can be depressed by adding citric acid, that acts as buffering and complexing agent. This leads to a lower iron content of the deposits. The Fe/Pt ratio close to one that is needed for hard magnetic properties can, however, only be achieved with a significant incorporation of iron hydroxide.

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1. Introduction

$L1_0$ FePt hard magnetic films are interesting candidates for the development of magnetic microelectromechanical systems, such as microactuators or micromotors. In contrast to physical deposition methods, electrodeposition is an economic and efficient route to prepare such films with a thickness in the micrometer range.

In previous works, FePt films with the desired Fe/Pt ratio close to one could be prepared by adjusting the deposition potential [1–3]. FePt electrodeposition has been proven to deviate strongly from normal codeposition behavior [2,4]. On one hand, Fe is incorporated in the films at potentials well above the equilibrium potential of Fe deposition. This has been discussed with respect to Fe underpotential deposition due to FePt alloy formation [2]. On the other hand, from −0.4 V vs. SCE on, oxygen is detected in the films [4,2]. The amount of oxygen increases when lowering the deposition potential and scales with the Fe content. It reaches a maximum of 30 at.% O at −0.78 V vs. SCE, where the Fe/Pt ratio of one is achieved. To account for the oxygen incorporation, iron hydroxide formation was proposed in addition to the underpotential model [4].

The oxygen content strongly influences the magnetic properties that can be achieved after annealing the films [1,5]. When the annealing needed for the $L1_0$ phase formation is carried out in hydrogen atmosphere, the oxygen content is reduced to 10 at.% [6]. The remaining iron oxides still limit the magnetic moment. At the same time, because of their fine distribution, the oxides can hinder grain growth. The resulting nanoscaled microstructure is of benefit for the hard magnetic properties, so that in electrodeposited FePt films a high coercivity of 1.1 T (after 10 min at 600 °C), but also a high remanence of 0.8 T (after 120 min at 400 °C) can be achieved [1,7].

With this background it is important to understand the mechanism of oxygen incorporation in order to control the film properties. The significant oxygen incorporation during FePt electrodeposition is also interesting from a fundamental point

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[*] Corresponding author at: IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany. Tel.: +49 351 4659 273; fax: +49 351 4659 471.
E-mail address: k.leistner@ifw-dresden.de (K. Leistner).

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of view, as it is not observed in similar systems as the Co–Pt or Ni–Pt system [8,9]. During Fe electrodeposition, oxygen incorporation is often correlated to Fe(III)-hydroxide formation, when Fe^{3+} ions are present in the electrolyte due to oxidation of Fe^{2+} by the surrounding air or by the anode [10]. However, unlike during single metal or transition metal alloy deposition, the oxygen incorporation in Fe–Pt is insensitive to measures that minimize the Fe^{3+} content in the electrolyte, as separation of anolyte and catholyte, prereducing procedures, and atmosphere control [2,4]. Previous studies have explained the oxygen incorporation in Fe–Pt by the formation of iron hydroxides due to a local pH increase at the cathode that results from strongly catalyzed hydrogen evolution on freshly deposited Pt [4,11]. The kind of iron hydroxide, however, could not be identified.

In this study, rotating disc electrode measurements have been performed for a further understanding of the electrode processes. Mössbauer spectroscopy was used to identify the oxidation state of Fe in as deposited Fe–Pt–O films. This information in combination with the measured stoichiometry allows to discuss the coexistance of different phases. Together with measurements of the Fe^{3+} content in the Fe–Pt electrolyte, a more detailed mechanism of the hydroxide incorporation is proposed.

2. Experimental

The electrolyte contained 0.001 mol/l H_2PtCl_6, 0.1 mol/l $FeSO_4$ and 0.525 mol/l Na_2SO_4, the pH was adjusted to 3 by adding H_2SO_4. Current density–potential curves under different convective conditions were measured using a rotating disc electrode (RDE) EDI 101 from Radiometer Copenhagen. In the RDE, a Cu rod, that had been polished at the front side, was pressed in the opening of the PTFE cylinder plane to the PTFE surface and served as the working electrode. As counter electrode a Pt sheet was used, the reference electrode was a saturated calomel electrode (SCE, 241 mV_{SHE}).

For film deposition, the working electrode consisted of a Si wafer coated with a W–Ti barrier and 100 nm Cu. To avoid dissolution of Cu, the working electrode was immersed into the electrolyte with the potential applied. N_2 gas flow was adjusted underneath the cathode to intermix the electrolyte and increase the deposition rate. The depositions were carried out potentiostatically for 30 min using an EG&G Potentiostat/Galvanostat Model 263A.

The integral film composition was measured by energy dispersive X-ray spectroscopy (EDX, EDAX system for SEM Philips XL 20). Phase analysis was carried out by means of Conversion Electron Mössbauer Spectroscopy (CEMS). The spectra were taken at room temperature with a $^{57}Co/Rh$ source (activity 400 MBq) and a constant acceleration drive. The conversion and Auger electrons were detected in a He/CH_4 gas-flow proportional counter. The spectra were stored in a multichannel scaler with 1024 channels and fitted according to a least squares fit routine by superimposing Lorentzian lines [12]. Velocity calibration was performed at room temperature with a 25 μm α-Fe foil, and all isomer shifts are related to the latter. The information depth of CEMS is about 150 nm [12].

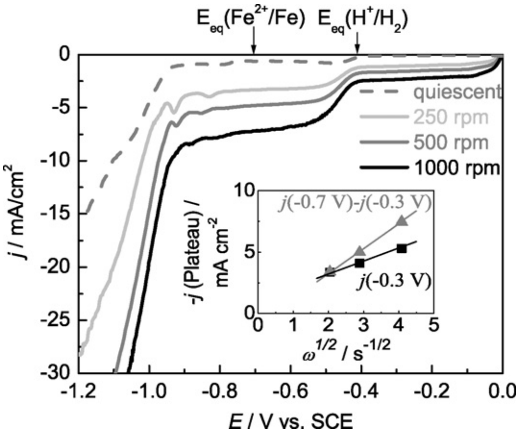

Fig. 1. $j(E)$ curves measured at a rotating disc electrode for different rotating speeds in 0.001 mol/l H_2PtCl_6, 0.1 mol/l $FeSO_4$and 0.525 mol/l Na_2SO_4 at a pH of 3.0, sweep rate 2 mV/s. The inset shows the current density attributed to the reduction of the Pt complex (−0.3 V) and the current density attributed to the hydrogen evolution reaction (at −0.7 V, after substraction of the current originating from the reduction of the Pt complex) vs. the square root of the angular velocity.

The amount of Fe^{2+} in the electrolyte has been determined by spectrophotometry using *o*-phenanthrolin that forms an orange-red complex with Fe^{2+} (E_{max} at $\lambda = 510$ nm). In order to obtain the total amount of Fe ions, Hydroquione has been added to the electrolyte in a separate experiment to reduce all Fe^{3+} to Fe^{2+}, that can then again be identified with *o*-phenanthrolin. The comparison between the amount of Fe^{2+} (without hydroquione treatment) and the total amount of Fe ions gives the amount of Fe^{3+} in the electrolyte. The characterization has been performed at different times after electrolyte preparation. As this measurement technique is only calibrated for low concentrations, the electrolyte had been diluted with a ratio of 1:100.

3. Results and discussion

The current density–potential curves obtained on the RDE under quiescent conditions and at different rotating speeds are plotted in Fig. 1. For quiescent conditions, the curve is comparable to the one obtained in an electrochemical quartz crystal microbalance (EQCM) setup that had been discussed in a previous contribution [11]. Following the EQCM measurements, the very small current density at potentials down to −0.4 V can be attributed to the reduction of the Pt complex. Hydrogen evolution by proton reduction starts at −0.4 V and reaches a plateau around −0.55 V. In the further course of the curve, the current density increases again at −0.74 V and then reaches a step that is followed by another current density increase at −0.92 V. According to the EQCM measurements, the latter is due to Fe overpotential deposition. The current density increase at −0.74 V is accompanied by an anomalous mass change and has thus been discussed as being due to Fe ion reduction in combination with Fe hydroxide formation [11].

When the disc electrode is rotated, the current density increases in comparison to quiescent conditions. Especially the current density in the plateau regions of the reduction of the